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Possible clustering mechanisms have been studies in two systems (i) intermetallic spin glass compound $Co^{x}Ga^{(1-x)}$ and (ii) amorphous magnetic ribbons of general composition $(Fe,Co)_{(1-x)}(B,Si)_{x}$ In the CoGa system evidence for vacancy clustering has been found following bombardment by Ar^{+} ions, this gives rise to dislocation dipoles up to 0.5um in length. Annealing or magnetic annealing of the amorphous ribbons may produce ordering of interstitial boron, phosphorus or silicon atoms or clustering of separate amorphous phases: in either casw uniaxial anisotropy is likely to be induced. Ion, proton and electron irradiation of amorphous materials can produce similary effects. Annealing above the crystallization temperature results in precipitation of second crystalline phases.

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MICROANALYSIS OF ATOMIC CLUSTERING IN ELECTROMAGNETIC MATERIALS

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Abstract

Possible clustering mechanisms have been studied in two distinct systems (i) quenched and slow cooled samples of the intermetallic spin glass compound Co_xGa_{1-x} ($0.5 < x < 0.55$) and (ii) amorphous magnetic ribbons of general composition $(Fe,Co)_{1-x}(B,Si)_x$ with $0.14 < x < 0.26$.

In the CoGa system evidence for vacancy clustering has been found following bombardment by 5 KeV Ar^+ ions. The clustering ultimately gives rise to distinctive dislocation dipoles which may be up to 0.5 μm in length.

Annealing or magnetic annealing of the amorphous ribbons below the crystallization temperature may produce ordering of interstitial boron, phosphorus or silicon atoms or even clustering of separate amorphous phases: in either case structurally dependent magnetic properties or more likely a uniaxial anisotropy is likely to be induced. Ion (Ar^+), proton and electron irradiation of amorphous materials can also produce effects similar to those of annealing.

Annealing above the crystallization temperature results in precipitation of second crystalline phases. The products and morphology of the second phases depend on initial ribbon composition and method of annealing.

MICROANALYSIS OF ATOMIC CLUSTERING IN ELECTROMAGNETIC STRUCTURE

AFOSR 80-005

I. Introduction

Clustering mechanisms are a common and important feature of many diverse physical systems. In this report we describe some clustering mechanisms that have been studied in two dissimilar electromagnetic materials.

The first is the intermetallic compound Co_xGa_{1-x} which forms the ordered B2 type structure (CsCl). For $x > 0.55$, the compounds exceed the percolation limit and become ferromagnetic. Quenched compounds in the composition range $0.5 < x < 0.55$ are reported to possess a spin glass behaviour. This behaviour has been attributed to the formation of superparamagnetic clusters of Co spins some 60 Å in size. This 'magnetic' clustering, detected by neutron diffraction, should not be confused with a physical segregation or diffusion of Co atoms. However it is possible that atomic diffusion together with changes of short range order do occur in spinglass materials. Indeed it has been suggested that they constitute the origin of ageing effects observed in Cu-Mn alloys [1].

A major part of our work has been directed towards an electron microscope study of clustering in CoGa compounds. No direct evidence for precipitation of Co was found in the microscope (although Hall effect measurements on AuMn at low temperatures may indicate clustering). (see footnote below*). On the other hand we have microscope evidence for the clustering of point defects. This phenomenon is promoted by ion bombardment. These results on defects are important because they are known to affect the magnetic behaviour of CoGa (2).

* In the spin glass state, spin coupling is rather weak and easily disrupted by both temperature and large magnetic fields: this is confirmed by Hall effect and magnetoresistance measurements in fields < 100 gauss. Results indicate significantly different behaviour of the coefficients compared with their high field counterparts. This work is being developed further.

The second main thrust of our investigation concerns the magnetic and structural properties of melt spun amorphous ribbons. In our work we have concentrated upon precipitation phenomena associated with incipient crystallization. It is known that segregation can influence magnetic properties such as coercivity. Results are presented in section 2.

2. Results

2.1 Ion Bombardment of CoGa specimens

The bombardment of CoGa alloys by 5 keV Ar^+ ions produces prominent features as observed in transmission electron microscope images. The features, which appear in all specimens independent of heat treatment and composition, consist of irregular lines up to 0.5μm in length and possess asymmetric contrast. Frequently they run in two perpendicular directions. The physical origin of these features has proved problematic and several suggestions have been proposed, e.g. antiphase boundaries. However their origin is certainly crystallographic and at the same time associated with the bombardment of ion beams. A similar contrast has been observed in gold films and attributed to dislocation dipoles. We believe a similar explanation is valid in the case of CoGa and may be understood as follows.

Incident Ar^+ ions of 5 keV create Frenkel defects in the Co and Ga sublattices. After an initial recombination the remaining interstitials diffuse away to leave a small residual number of monovacancies. These condense to form highly mobile divacancies and stable trivacancies. A critical stage is now reached because in order to account for the ultimate length of the dipoles it is essential that newly formed monovacancies condense preferentially on to already formed trivacancies (to form clusters) rather than create new trivacancies. Jouffrey (3) has shown that the former process can occur. Nevertheless the possibility of forming, by a mono-vacancy condensation process, defects some hundreds of atomic spacings in size is remote. This means that the newly formed clusters must themselves coalesce and condense to produce large vacancy clusters and associated dislocation loops. However, attractive forces between neighbouring defects will only result in condensation if they are contained in planes but a few interatomic distances apart (4). Otherwise a mutual attraction will bring them into parallel alignment - thus forming a stable dipole. It is proposed that the dipoles observed in our work were created in this way.

There still remain problems associated with this mechanism. Why are there so many dipoles and comparatively fewer single dislocation lines? Why do the dipoles appear to form along reasonably well defined crystallographic axes - $\langle 100 \rangle$ directions? On the other hand positive evidence for the physical pressure of Ar ions has been obtained from in-situ annealing experiments in the microscope. At higher temperature new defects are observed which can be identified with bubbles of argon gas.

2.2 Clustering in amorphous metallic ribbons

Amorphous metallic alloys are metastable and can be transformed with the possible formation of a second amorphous phase, or more commonly a crystalline phase by thermal activation or particle irradiation (5). Prior to this identifiable crystallization, it is thought that structural re-arrangements can occur with the modification of topological or chemical short range order and the redistribution of free volume in the material. Hence it is conceivable that phase separation could occur. Indeed such effects have been observed in large angle diffraction experiments on GdCo films (6) and in small angle X-ray scattering of P segregation in FeNiPB amorphous ribbons. (7).

In the section above we distinguished between magnetic clustering and physical clustering. A similar disparity may occur in amorphous ribbons. If an amorphous ribbon of composition $Co_{75}Fe_5B_{20}$ is annealed in a magnetic field below the crystallization temperature then a uniaxial anisotropy may be induced. The origin of this anisotropy is directional pair ordering. The theory behind the effect is well known but lengthy(8). Suffice it to say that under the condition of negative non-magnetic interaction energy between like pairs of atoms, there is a tendency towards clustering. Such a condition is believed to exist in amorphous ribbons. This does not mean the formation of a crystalline phase but, rather, the segregation into two amorphous phases. In other words the clustering is short range as opposed to long range superlattice formation, which occurs with a positive non-magnetic interaction energy.

We have carried out long term (25 hr) annealing experiments in small fields below the crystallization temperatures of a number of alloys. In no case so far have we found evidence, using electron microscopy, for segregation into distinct amorphous phases. We may conclude that the effect is so small as to be undetectable in the transmission microscope. A probable clue to the correctness of this conclusion is contained within the work of Luborsky and Walter (9) who estimate the 'segregation' temperature for Fe-Ni-B alloys as 3900K. Despite this high value (well above the actual crystallization temperature for the alloy) uniaxial anisotropy is induced at a temperature of 598K.

However we have found that measurements of magnetic coercivity in amorphous ribbons, isothermally annealed at temperatures below the normal crystallization temperature (10), do show a dependence on the time of anneal. This may be associated with structural relaxation effects or phase separation and clustering accompanying significant chemical short range order. We expect that, with the acquisition of a new transmission electron microscope (TEM), high resolution structural studies will enable us to correlate these changes in magnetic properties with any clustering. Small angle X-ray scattering measurements on these materials are also in progress at the nearby S.E.R.C. Daresbury Synchrotron Facility.

As in the case of crystalline CoGa alloys, ion irradiation is seen to cause irradiation damage in amorphous alloys. Large doses (5 keV Ar^+ ions, at > 5×10^{16} ions cm^2) produce easily observable voids or bubbles $\sim$ 10 nm in diameter (11). One of the aims of this investigation of ion and neutron irradiation in amorphous ribbons is to identify the origin and mechanism of irradiation-induced clustering and free volume redistribution in these materials.

Finally we turn to annealing experiments conducted at a temperature which does lead to the formation of well defined second crystalline phases. From our many results in this area we may conclude the following (i) the onset of crystallization is marked by the formation of nuclei of iron or cobalt depending on particular composition (ii) the subsequent stages of crystallization involve the formation of borides, phosphides etc. depending upon the quanity of glass-forming elements (111) the morphology of the crystallized nuclei is composition dependent (IV) the morphology of the crystallized nuclei for a given composition depends upon the method of annealing, i.e. whether furnace-annealed or annealed in-situ in the electron microscope.

It is clear that the difference between furnace and microscope annealed samples must be attributed to the thinness of the specimens used in the latter process.

3. Conclusion

Specimens of the crystalline spin glass Co_xGa_{1-x} and the amorphous metallic glass system $(Fe,Co)_{1-x}(B,Si)_x$ have been subject to irradiation by Ar^+ ions. In both cases evidence for some sort of clustering was forthcoming. For CoGa this results in the formation of an extended network of dislocation dipoles. The effect of these defects upon the spin glass behaviour of CoGa is as yet unknown but it is proposed to investigate this aspect further via a study of transport properties. Annealing of irradiated CoGa produces blisters of argon gas. Similar blistering is observed in annealed irradiated metallic glasses but it is believed that the irradiation also causes structural changes leading to a redistribution of free volume. At present we are investigating the effects of neutron irradiation on metallic glasses. The Curie point and crystallization temperature are altered as a function of neutron dose.

Apart from irradiation effects metallic glasses have been subjected to various heat and magnetic annealing treatments. Crystallization kinetics and crystalline phases are a function of composition and method of annealing.

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Conferences Attended

Intermag 82, Montreal 1982

MMM Conference, Atlanta, 1981

Ion Beam Modification of Materials, Grenoble 1982

Current Research in Magnetism, London 1982

Rapidly Quenched Metal Conference, Open University, Milton Keynes 1982.

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